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### (54) Process for preparing polyolefin catalysts

Verfahren zur Herstellung von Polyolefinkatalysatoren

Procédé pour la préparation de catalysateurs de polyoléfines

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(56) References cited:  
**EP-A- 0 452 920** **US-A- 4 659 685**

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## Description

[0001] This invention relates to a method for preparing catalysts for producing polyolefins having a bi- or multimodal molecular weight distribution.

[0002] Polyolefins having a multimodal molecular weight distribution (MWD) can be converted into articles by extrusion molding, thermoforming, rotational molding, etc. and have advantages over typical polyolefins lacking the multimodal MWD. Polyolefins having a multimodal MWD may be processed more easily, i.e. they can be processed at a faster throughput rate with lower energy requirements and at the same time such polymers evidence reduced melt flow perturbations and are preferred due to improved properties for applications such as high strength films.

[0003] There are several known methods for producing polyolefins having a multimodal MWD; however, each method has its own disadvantages. Polyolefins having a multimodal MWD can be made by employing two distinct and separate catalysts in the same reactor each producing a polyolefin having a different MWD; however, catalyst feed rate is difficult to control and the polymer particles produced are not uniform in size, thus, segregation of the polymer during storage and transfer can produce non-homogeneous products. A polyolefin having a bimodal MWD can also be made by sequential polymerization in two separate reactors or by blending polymers of different MWD during processing; however, both of these methods increase capital cost.

[0004] European Patent N° 0128045 discloses a method of producing polyethylene having a broad molecular weight distribution and/or a multimodal MWD. The polyethylenes are obtained directly from a single polymerization process in the presence of a catalyst system comprising two or more metallocenes each having different propagation and termination rate constants, and aluminoxane.

[0005] There are certain limits to the known methods for preparing bimodal molecular weight distribution or multimodal molecular weight distribution polyolefins. Even under ideal conditions the gel permeation chromatograph curves don't show a marked bimodal MWD of the polyolefin. The MWD and shear rate ratios of the polymer and the catalyst activity disclosed in the known methods are rather poor. Further the known metallocene catalyst systems for producing bimodal MWD use aluminoxane as cocatalyst during the polymerization which causes severe fouling inside the reactor and renders the use of such a type of catalyst in continuous processes almost impossible.

[0006] It is therefore not surprising that none of the known methods for producing a multimodal MWD polyolefin from a single polymerization process in the presence of a catalytic system comprising at least two metallocenes have been developed at an industrial scale.

[0007] It is an object of the present invention to provide for a new process for preparing a catalyst for preparing polyolefins having a multimodal molecular weight distribution.

[0008] In accordance with the present invention, a process is provided for preparing a supported catalyst-component for use in the preparation of polyolefins having a multimodal or at least bimodal molecular weight distribution comprising an alumoxane and at least two metallocenes containing the same transition metal and selected from mono, di, and tricyclopentadienyls and substituted cyclopentadienyls of a transition metal wherein at least one of the metallocenes is bridged and at least one of the metallocenes is unbridged, characterized by the fact that the supported catalyst-component is obtained by mixing together the unbridged metallocene alumoxane supported catalyst with the bridged metallocene alumoxane supported catalyst.

[0009] While alumoxane can be used as cocatalyst, the Applicant has found that it was not necessary to use alumoxane as cocatalyst during the polymerization procedure for preparing polyolefins according to the process of the present invention. Further the use of alumoxane as a cocatalyst during the polymerization may lead to the fouling of the reactor.

According to a preferred embodiment of the present invention, one or more cocatalysts represented by the formula  $MR_x$  are used, wherein M is a metal selected from Al, B, Zn, Li and Mg, each R is the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable cocatalysts are trialkylaluminium selected from trimethylaluminium, triethylaluminium, triisobutylaluminium, tri-n-hexylaluminium or tri-n-octylaluminium, the most preferred being triisobutylaluminium.

[0010] The broadness of the molecular weight distribution and the average molecular weights can be controlled by selecting the preparation of the catalyst system. In a preferred embodiment of the present invention, this control is also performed by the introduction of some amount of hydrogen during polymerization. Another preferred embodiment of the present invention implies the use of a comonomer for this control; examples of comonomer which can be used include 1-olefins such as 1-butene, 1-hexene, 1-octene, 4-methyl-pentene, and the like, the most preferred being 1-hexene.

[0011] It has unexpectedly been found that the polymerization process can be conducted under slurry phase polymerization conditions and this constitutes a real advantage of the process of the present invention. While slurry phase polymerization may be conducted under well known operating conditions, it is preferred that it is operated at a temperature of about 20 to 125°C and a pressure of about 0.1 to 5.6 MPa for a time between 10 minutes and 4 hours.

[0012] Another advantage of the present invention is that a continuous reactor can be used for conducting the po-

lymerization. This continuous reactor is preferably a loop reactor. During the polymerization process, the olefin monomer(s), the catalytic system, the cocatalyst and a diluent are flowed in admixture through the reactor.

**[0013]** A further advantage of the present invention is that the bulk density of the polymer obtained by the catalyst preparation process of the present invention is particularly high. The bulk density is an important characteristic of the polymer. The bulk density, commonly expressed in terms of grams per cubic centimeters, should be relatively high. If the bulk density is too low, the polymer will tend to be fluffy and will tend to cause plugging and handling problems in the product transfer system. Low bulk densities mean problems for fluff packaging and for the extrusion processing. This is particularly important in a continuous or a semi-continuous polymerization where plugging of the withdrawal outlet or another point in the polymerization system can cause serious interruptions in production schedules.

**[0014]** When hydrogen is used it is preferred that the relative amounts of hydrogen and olefin introduced into the polymerization reactor be within the range of about 0.001 to 15 mole percent hydrogen and 99.999 to 85 mole percent olefin based on total hydrogen and olefins present, preferably about 0.2 to 3 mole percent hydrogen and 99.8 to 97 mole percent olefin.

**[0015]** It is preferred that the polymerization reaction be run in a diluent at a temperature at which the polymer remains as a suspended solid in the diluent. Diluents include, for example, isobutane, n-hexane, n-heptane, methylcyclohexane, n-pentane, n-butane, n-decane, cyclohexane and the like. The preferred diluent is isobutane.

**[0016]** The olefin monomer used to produce a polyolefin of bimodal or multimodal molecular weight distribution in which each polymer particle contains both high and low molecular weight polymer molecules is preferably selected from ethylene and mono-1-olefins (alpha olefins), preferably mono-1-olefins having from 2 to 10 carbon atoms including for example, 4-methyl-1-pentene. More preferably these mono-1-olefins are selected from the group consisting of ethylene, propylene, and mixtures thereof; ethylene being the most preferred.

**[0017]** According to the present invention, the supported catalyst-component used in the process for producing polyolefins having multimodal molecular weight distribution can be made by any known method as long as it comprises an alumoxane and at least two metallocenes containing the same transition metal wherein at least one of the metallocenes is bridged and at least one of the metallocenes is unbridged.

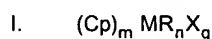
**[0018]** Known processes of producing these types of catalysts are disclosed in European Patent N° 0206794.

**[0019]** This patent discloses a catalyst-component comprising the reaction product of at least one metallocene and alumoxane in the presence of a support material thereby providing a supported metallocene-alumoxane reaction product as the sole catalyst component.

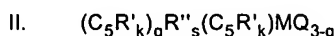
**[0020]** Another supported catalyst-component using two metallocenes wherein one of the metallocenes is bridged and the other metallocene is unbridged is also disclosed in European Patent n° 0452920 which teaches a catalyst system for the preparation of polyolefins having specific rheologic properties.

**[0021]** The metallocenes used in the catalyst preparation process of the present invention are organometallic coordination compounds which are cyclopentadienyl derivatives of a Group 4b, 5b or 6b metal of the Periodic Table and include mono, di and tricyclopentadienyls and their derivatives of the transition metals. Particularly desirable are the metallocene of a Group 4b and 5b metal such as titanium, zirconium, hafnium and vanadium.

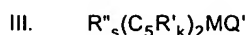
**[0022]** The preferred metallocenes can be represented by the general formulae:



wherein Cp is a cyclopentadienyl ring, M is a Group 4b, 5b or 6b transition metal, R is a hydrocarbyl group or hydrocarboxy having from 1 to 20 carbon atoms, X is a halogen, and m = 1-3, n = 0-3, q = 0-3 and the sum of m+n+q will be equal to the oxidation state of the metal.



and



wherein  $(\text{C}_5\text{R}'_k)$  is a cyclopentadienyl or substituted cyclopentadienyl, each R' is the same or different and is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical containing from 1 to 20 carbon atoms or two carbon atoms are joined together to form a  $\text{C}_4\text{-C}_6$  ring, R'' is a  $\text{C}_1\text{-C}_4$  alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical bridging two  $(\text{C}_5\text{R}'_k)$  rings, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms, hydrocarboxy radical having 1-20

carbon atoms or halogen and can be the same or different from each other, Q' is an alkylidene radical having from 1 to about 20 carbon atoms, s is 0 or 1, g is 0, 1 or 2, s is 0 when g is 0, k is 4 when s is 1 and k is 5 when s is 0, and M is as defined above.

**[0023]** Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like.

Exemplary halogen atoms include chlorine, bromine, fluorine and iodine and of these halogen atoms, chlorine is preferred.

Exemplary hydrocarboxy radicals are methoxy, ethoxy, propoxy, butoxy, amyloxy and the like.

Exemplary of the alkylidene radicals is methylidene, ethylidene and propylidene.

**[0024]** According to a preferred embodiment of the present invention, the catalyst-component comprises at least two metallocenes deposited on a separate support wherein :

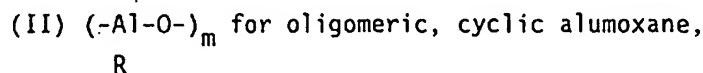
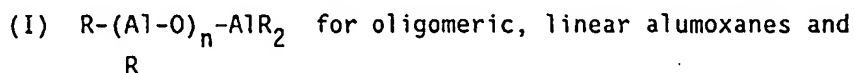
- at least one of the metallocenes is unbridged and is represented by the formula  $(Cp)_2MX_2$  wherein each Cp is the same or different and is selected from substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium and X, which is the same or different, is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms or a halogen.
- at least one of the metallocenes is bridged and is represented by the formula  $R''(Cp)_2MX_2$  wherein each Cp is the same or different and is selected from substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium, X, which is the same or different, is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms or a halogen and R'' is a C<sub>1</sub>-C<sub>4</sub> alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical bridging two (Cp) rings.

**[0025]** Preferably, in the above-identified formulae, for the unbridged metallocene Cp is a substituted or unsubstituted cyclopentadienyl or indenyl, M is zirconium, titanium or hafnium and X is Cl or CH<sub>3</sub>, and for the bridged metallocene Cp is a substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium, X is Cl or CH<sub>3</sub> and R'' is an ethylene radical or silicon.

**[0026]** Preferably, the unbridged metallocene is a bis(cyclopentadienyl) zirconium dichloride and the bridged metallocene is an ethylene-bis(indenyl) zirconium dichloride.

**[0027]** The molar ratio of the unbridged metallocenes to the bridged metallocenes can vary over a wide range, and in accordance with the present invention, the only limitation on the molar ratio is the breadth of the molecular weight distribution (MWD) and the degree of bimodality desired in the product polymer. Preferably, the unbridged to bridged metallocenes molar ratio will be between 10:1 and 1:10, preferably between 5:1 and 1:5, more preferably between 4:1 and 2:1.

**[0028]** The alumoxanes used in the process of the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula :



wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C<sub>1</sub>-C<sub>8</sub> alkyl group and preferably methyl. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of linear and cyclic compounds is obtained.

**[0029]** The support used in the process of the present invention can be any of the solid, particularly, porous supports such as talc, inorganic oxides, and resinous support materials such as polyolefin.

Preferably, the support material is an inorganic oxide in its finely divided form.

Suitable inorganic oxide materials which are desirably employed in accordance with this invention include Group 2a, 3a, 4a or 4b metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins such as finely divided polyethylene.

Preferably, the support is a silica having a surface area comprised between 200 and 600 m<sup>2</sup>/g and a pore volume

comprised between 0.5 and 3 ml/g.

[0030] The amount of alumoxane and metallocenes usefully employed in the preparation of the solid support catalyst can vary over a wide range. Preferably the aluminium to transition metal mole ratio is comprised between 1:1 and 100:1, preferably between 5:1 and 50:1.

[0031] According to the present invention, the supported catalyst-component is prepared by mixing together the unbridged metallocene alumoxane supported catalyst with the bridged metallocene alumoxane supported catalyst. Preferred solvents include mineral oils and the various hydrocarbons which are liquid at reaction temperatures and which do not react with the individual ingredients. Illustrative examples of the useful solvents include the alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane and cyclohexane, and aromatics such as benzene, toluene, ethylbenzene and diethylbenzene. Preferably the support material is slurried in toluene and the metallocene and alumoxane are dissolved in toluene prior to addition to the support material.

#### 1. Catalyst preparation

[0032] The two supports used are MAO supported silica having a surface area of 322 m<sup>2</sup>/g (GRACE 952). This silica is further prepared by drying in high vacuum on a schlenk line for three hours to remove the physically absorbed water and then suspended in toluene to react with methyl alumoxane (MAO) for three hours at the reflux temperature. Finally it is cooled and washed three times with toluene to remove the unreacted MAO.

(a) a solution of (Cp)<sub>2</sub>ZrCl<sub>2</sub> in toluene is deposited on the first support by stirring the resulting suspension for one hour at ambient temperature. The supernatant liquid was filtered off and the remaining solid was dried under vacuum after being washed three times with toluene.

(b) a solution of ethylene (Ind)<sub>2</sub>ZrCl<sub>2</sub> in toluene is deposited on the second support by stirring the resulting suspension for one hour at ambient temperature. The supernatant liquid was filtered off and the remaining solid was dried under vacuum after being washed three times with toluene.

(c) the two separately obtained supported metallocenes (a) and (b) were mixed together in a 2:1 weight ratio ((a): (b)).

#### 2. Polymerization procedure

[0033] The reactor used in all examples has a capacity of 35 liters and is continuously agitated. This continuous reactor is first filled with isobutane at a pressure of 40 bars. Then, as indicated in figure 1, a suspension of supported catalyst (1), isobutane (2), TIBAL (3), hexene (4), ethylene (5) and hydrogen (6) are continuously introduced into the reactor. The polymers are recovered at (9). All polymers were analyzed by Gel Permeation Chromatography (GPC-WATERS MILLIPORE) and Differential Scanning Calorimetry (DSC). The graphs are given in figures 2 to 20 (figures 2 to 20 respectively correspond to examples 5 to 23 of table 2). "D" represents the ratio Mw/Mn (MWD), "D'" the ratio Mz/Mw and "A" the area under the curve. The polymerization conditions and the polymer properties are given in table 2.

TABLE I

| Ex | Cata  | TIBAL | i-C <sub>4</sub> | C <sub>2</sub> | C <sub>6</sub> | H <sub>2</sub> | Bulk (1) | MI <sub>2</sub> (2) | HLMI (3) | SRR (4) | D (5)  | Mz    | Mw    | Mn    | MWD  |
|----|-------|-------|------------------|----------------|----------------|----------------|----------|---------------------|----------|---------|--------|-------|-------|-------|------|
|    | (g/h) | (g/h) | (kg/h)           | (kg/h)         | (cc/h)         | (Nl/h)         | (g/cc)   | (g/10')             | (g/10')  |         | (g/cc) | x10E3 | x10E3 | x10E3 |      |
| 5  | 4.5   | 7.2   | 18               | 3              | 0              | 33             | 0.38     | 0.22                | 45.9     | 204     | 0.965  | 2218  | 254   | 7.7   | 33.0 |
| 6  | 4.5   | 7.2   | 18               | 2.5            | 0              | 14             | 0.37     | 0.12                | 30.6     | 251     | 0.963  | 2492  | 300   | 9.0   | 33.3 |
| 7  | 4.5   | 7.2   | 18               | 2.5            | 0              | 15             | 0.37     | 0.05                | 13.9     | 259     | 0.965  | 2699  | 357   | 10.2  | 35.0 |
| 8  | 4.5   | 7.2   | 18               | 2.5            | 0              | 15             | 0.35     | 0.05                | 13.6     | 300     | 0.964  | 2868  | 381   | 10.2  | 37.4 |
| 9  | 4.5   | 7.2   | 16               | 2              | 268            | 15             | 0.38     | 0.07                | 15.7     | 225     | 0.958  | 2644  | 337   | 9.4   | 35.7 |
| 10 | 4.5   | 7.2   | 16               | 2              | 265            | 15             | 0.39     | 0.09                | 23.9     | 266     | 0.959  | 2486  | 323   | 9.4   | 34.5 |
| 11 | 4.5   | 7.2   | 16               | 2              | 270            | 15             | 0.39     | 0.08                | 24.0     | 312     | 0.958  | 2390  | 307   | 9.0   | 34.1 |
| 12 | 4.5   | 7.2   | 16               | 2              | 274            | 15             | 0.39     | 0.11                | 24.8     | 232     | 0.958  | 2402  | 308   | 9.1   | 33.8 |
| 13 | 4.5   | 7.2   | 16               | 2              | 268            | 15             | 0.39     | 0.10                | 24.5     | 255     | 0.959  | 2437  | 325   | 9.7   | 33.6 |

## Catalyst preparation (B)

- (1) Bulk Density (ASTM-D-1895)
- (2) Melt Index (ASTM-D-1238-89A)
- (3) High Load Melt Index (ASTM-D-1238-89A)
- (4) Shear Rate Response (HLMI/MI<sub>2</sub>)
- (5) Density (ASTM-D-1505-85)

TIBAL triisobutylaluminium, i-C<sub>4</sub> isobutane, C<sub>2</sub> ethylene, C<sub>6</sub> hexene

TABLE I (continued)

| Ex | Cata  | TIBAL | i-C <sub>4</sub> | C <sub>2</sub> | C <sub>6</sub> | H <sub>2</sub> | Bulk (1) | MI <sub>2</sub> (2) | HLMI (3) | SRR (4) | D (5)  | Mz    | Mw    | Mn    | MWD  |
|----|-------|-------|------------------|----------------|----------------|----------------|----------|---------------------|----------|---------|--------|-------|-------|-------|------|
|    | (g/h) | (g/h) | (kg/h)           | (kg/h)         | (cc/h)         | (Nl/h)         | (g/cc)   | (g/10')             | (g/10')  |         | (g/cc) | x10E3 | x10E3 | x10E3 |      |
| 14 | 4.5   | 7.2   | 18               | 2              | 0              | 0              | 0.30     | 0.16                | 11.8     | 74      | 0.951  | 2068  | 216   | 19.3  | 11.2 |
| 15 | 4.5   | 7.2   | 18               | 2              | 0              | 0              | 0.28     | 0.08                | 6.5      | 80      | 0.951  | 2569  | 264   | 26.3  | 10.0 |
| 16 | 4.5   | 7.2   | 18               | 2              | 0              | 0              | 0.28     | 0.14                | 9.6      | 69      | 0.951  | 1751  | 198   | 18.7  | 10.6 |
| 17 | 4.5   | 7.2   | 18               | 2.5            | 198            | 0              | 0.30     | 0.09                | 7.4      | 80      | 0.945  | 2419  | 270   | 27.0  | 10.0 |
| 18 | 4.5   | 7.2   | 18               | 2.5            | 200            | 0              | 0.30     | 0.07                | 6.1      | 94      | 0.941  | 2498  | 282   | 29.0  | 9.7  |
| 19 | 4.5   | 7.2   | 18               | 2.5            | 205            | 0              | 0.30     | 0.05                | 5.6      | 110     | 0.941  | 2488  | 288   | 30.1  | 9.6  |
| 20 | 4.5   | 7.2   | 18               | 2.5            | 207            | 0              | 0.30     | 0.05                | 5.1      | 97      | 0.939  | 2257  | 270   | 32.0  | 8.4  |
| 21 | 4.5   | 7.2   | 16               | 2              | 202            | 10             | 0.30     | 0.13                | 11.4     | 87      | 0.945  | 2341  | 250   | 18.3  | 13.7 |
| 22 | 4.5   | 7.2   | 16               | 2              | 210            | 10             | 0.30     | 0.11                | 9.1      | 78      | 0.946  | 2653  | 261   | 19.0  | 13.8 |
| 23 | 4.5   | 7.2   | 16               | 2              | 200            | 12             | 0.29     | 0.10                | 7.9      | 78      | 0.942  | 2162  | 247   | 23.6  | 10.5 |

## Catalyst preparation (B)

- (1) Bulk Density (ASTM-D-1895)
- (2) Melt Index (ASTM-D-1238-89A)
- (3) High Load Melt Index (ASTM-D-1238-89A)
- (4) Shear Rate Ratio (HLMI/MI<sub>2</sub>)
- (5) Density (ASTM-D-1505-85)

TIBAL triisobutylaluminium, i-C<sub>4</sub> isobutane, C<sub>2</sub> ethylene, C<sub>6</sub> hexene

## Claims

1. Process for preparing a supported catalyst-component for use in the preparation of polyolefins having a multimodal or at least bimodal molecular weight distribution comprising an alumoxane and at least two metallocenes containing the same transition metal and selected from mono, di, and tri-cyclopentadienyls and substituted cyclopentadienyls of a transition metal wherein at least one of the metallocenes is bridged and at least one of the metallocenes is unbridged, characterized by the fact that the supported catalyst-component is obtained by mixing together the unbridged metallocene alumoxane supported catalyst with the bridged metallocene alumoxane supported catalyst.
2. Process according to claim 1, wherein the support is a silica having a surface area comprised between 200 and 600 m<sup>2</sup>/g and a pore volume comprised between 0.5 and 3 ml/g.
3. Process according to claim 2 wherein each metallocene alumoxane supported catalyst is prepared by the process comprising the steps of
  - suspending the support material in a suitable inert hydrocarbon
  - reacting the support with the alumoxane
  - washing the support with a suitable inert hydrocarbon to remove the unreacted alumoxane
  - adding a solution of the metallocene in a suitable inert hydrocarbon solvent
4. The process of anyone of the preceding claims, wherein:
  - the unbridged metallocenes are represented by the formula (Cp)<sub>2</sub>MX<sub>2</sub> wherein each Cp is the same or different and is selected from substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium and X, that is the same or different, is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alylaryl, or aryl alkyl radical having 1-20 carbon atoms or halogen;
  - the bridged metallocenes are represented by the formula R"(Cp)<sub>2</sub>MX<sub>2</sub> wherein each Cp is the same or different and is selected from substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium and X, that is the same or different, is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alylaryl, or aryl alkyl radical having 1-20 carbon atoms or halogen and R" is a C1-C4 alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical bridging two Cp rings.
5. A process according to anyone of the preceding claims, wherein in the formula for the unbridged metallocene Cp is a substituted or unsubstituted cyclopentadienyl or indenyl, M is zirconium, titanium or hafnium and X is Cl or CH<sub>3</sub> and in the formula for the bridged metallocene, Cp is a substituted or unsubstituted cyclopentadienyl or indenyl or fluorenyl, M is zirconium, titanium or hafnium and X is Cl or CH<sub>3</sub> and R" is an ethylene radical or silicon.
6. A process according to claim 5 wherein the unbridged metallocene is a bis (cyclopentadienyl) zirconium dichloride and the bridged metallocene is an ethylene-bis(indenyl) zirconium dichloride.

## Patentansprüche

1. Verfahren zum Herstellen einer unterstützten Katalysator-Komponente für Verwendung bei der Herstellung von Polyolefinen mit einer multimodalen oder mindestens bimodalen Molekulargewichtsverteilung, umfassend ein Alumoxan und mindestens zwei Metallocene, enthaltend das gleiche Übergangsmetall und ausgewählt aus Mono-, Di- und Tricyclopentadienylen und substituierten Cyclopentadienylen eines Übergangsmetalls, wobei mindestens eines der Metallocene verbrückt ist, und mindestens eines der Metallocene nicht verbrückt ist, **dadurch gekennzeichnet**, daß die unterstützte Katalysator-Komponente erhalten wird durch Zusammenmischen des unterstützten nicht verbrückten Metallocen Alumoxan Katalysators mit dem unterstützten verbrückten Metallocen Alumoxan Katalysator.
2. Verfahren nach Anspruch 1, wobei der Träger ein Silika mit einem Oberflächenbereich, enthalten zwischen 200 und 600 m<sup>2</sup>/g und einem Porenvolumen, enthalten zwischen 0,5 und 3 ml/g ist.
3. Verfahren nach Anspruch 2, wobei jeder unterstützte Metallocen Alumoxan Katalysator hergestellt wird durch das Verfahren, umfassend die Stufen von



- Suspendieren des Trägermaterials in einem geeigneten inerten Kohlenwasserstoff,
- Umsetzen des Trägers mit dem Alumoxan,
- Waschen des Trägers mit einem geeigneten inerten Kohlenwasserstoff unter Entfernen des nicht umgesetzten Alumoxans,
- 5 - Hinzufügen einer Lösung des Metallocens in einem geeigneten inerten Kohlenwasserstofflösungsmittel.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei

- 10 - die nicht verbrückten Metallocene dargestellt sind durch die Formel  $(Cp)_2MX_2$ , wobei jedes Cp das Gleiche oder unterschiedlich ist und ausgewählt ist aus substituiertem oder unsubstituiertem Cyclopentadienyl, Indenyl oder Fluorenyl, M ist Zirkonium, Titan oder Hafnium, und X, das das Gleiche oder unterschiedlich ist, ist ein Hydrocarbylrest wie Aryl, Alkyl, Alkenyl, Alkylaryl oder Arylalkylrest mit 1-20 Kohlenstoffatomen oder Halogen;
- 15 - die verbrückten Metallocene sind dargestellt durch die Formel  $R''(Cp)_2MX_2$ , wobei jedes Cp das Gleiche oder unterschiedlich ist und ausgewählt ist aus substituiertem oder unsubstituiertem Cyclopentadienyl, Indenyl oder Fluorenyl, M ist Zirkonium, Titan oder Hafnium, und X, das das Gleiche oder unterschiedlich ist, ist ein Hydrocarbylrest wie Aryl-, Alkyl-, Alkenyl-, Alkylaryl- oder Arylalkylrest mit 1-20 Kohlenstoffatomen oder Halogen, und  $R''$  ist ein C1-C4 Alkylrest, ein Dialkylgermanium oder Silicium oder Siloxan, oder ein Alkylphosphin oder Aminrest, zwei Cp Ringe verbrückend.

- 20 5. Verfahren nach einem der vorhergehenden Ansprüche, wobei in der Formel für das nicht verbrückte Metallocen Cp ein substituiertes oder unsubstituiertes Cyclopentadienyl oder Indenyl ist, M ist Zirkonium, Titan oder Hafnium, und X ist Cl oder  $CH_3$ , und in der Formel für das verbrückte Metallocen ist Cp ein substituiertes oder unsubstituiertes Cyclopentadienyl oder Indenyl oder Fluorenyl, M ist Zirkonium, Titan oder Hafnium, und X ist Cl oder  $CH_3$ , und  $R''$  ist ein Ethylenrest oder Silicium.

- 25 6. Verfahren nach Anspruch 5, wobei das nicht verbrückte Metallocen ein Bis(cyclopentadienyl)zirkonumdichlorid ist, und das verbrückte Metallocen ist ein Ethylenbis(indenyl)zirkonumdichlorid.

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# Revendications

- 35 1. Procédé pour préparer un composant de catalyseur sur support à utiliser pour la préparation de polyoléfines ayant une distribution multimodale ou au moins bimodale des poids moléculaires comprenant un alumoxane et au moins deux métallocènes contenant le même métal de transition et choisis parmi les mono, di, et tri-cyclopentadiényles ou cyclopentadiényles substitués d'un métal de transition ou au moins l'un des métallocènes est ponté et au moins l'un des métallocènes n'est pas ponté, caractérisé par le fait que le composant de catalyseur sur support est obtenu en mélangeant ensemble le catalyseur de métallocène alumoxane sur support non ponté avec le catalyseur de métallocène alumoxane sur support ponté .

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2. Procédé selon la revendication 1 dans lequel le support est une silice ayant une aire de surface comprise entre 200 et 600  $m^2/g$  et un volume de poids compris entre 0,5 et 3  $ml/g$ .

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3. Procédé selon la revendication 2 dans lequel chaque catalyseur de métallocène alumoxane sur support est préparé par le procédé comprenant les étapes de:

- mise en suspension de la matière de support dans un hydrocarbure inerte adéquat
- faire réagir le support avec l'alumoxane
- laver le support avec un hydrocarbure inerte adéquat pour éliminer l'alumoxane n'ayant pas réagi
- 50 - ajouter une solution de métallocène dans un solvant d'hydrocarbure inerte adéquat.

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4. Procédé selon l'une quelconque des revendications précédentes dans lequel:

- les métallocènes non pontés sont représentés par la formule  $(Cp)_2MX_2$  où chaque Cp est le même ou différent et est choisi dans le groupe des cyclopentadiényles substitués ou non substitués, indényles ou fluorényles, M est du zirkonium, titane ou hafnium et X, qui est le même ou différent est un radical hydrocarbyle tel que aryle, alkyle, alkényle, alkylyle, ou arylalkyle ayant de 1-20 atomes de carbone ou un halogène;
- les métallocènes pontés sont représentés par la formule  $R''(Cp)_2MX_2$  où chaque Cp est le même ou différent

et est choisi dans le groupe des cyclopentadiényles substitués ou non substitués, indényles ou fluorényles, M est du zirconium, titane ou hafnium et X, qui est le même ou différent est un radical hydrocarbyle tel que aryle, alkyle, alkényle, alylaryle, ou arylalkyle ayant de 1-20 atomes de carbone ou un halogène et R" est un radical C1-C4 alkylène, un dialkylgermanium ou silicium ou siloxane, ou une alkylphosphine ou un radical amine pontant les deux anneaux Cp.

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5. Procédé selon l'une quelconque des revendications précédentes dans lequel la formule du métallocène Cp non ponté est un cyclopentadiényle ou indényle substitué ou non substitué, M est du zirconium, titane ou hafnium et X est Cl ou CH<sub>3</sub> et dans la formule du métallocène ponté, Cp est un cyclopentadiényle ou indényle ou fluorényle substitué ou non substitué, M est le zirconium, titane ou hafnium et X est Cl ou CH<sub>3</sub> et R" est un radical éthylène ou silicium.

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6. Procédé selon la revendication 5 dans lequel le métallocène ponté est un dichlorure de bis(cyclopentadiényl) zirconium et le métallocène ponté est un dichlorure d'éthylène-bis(indényl)zirconium.

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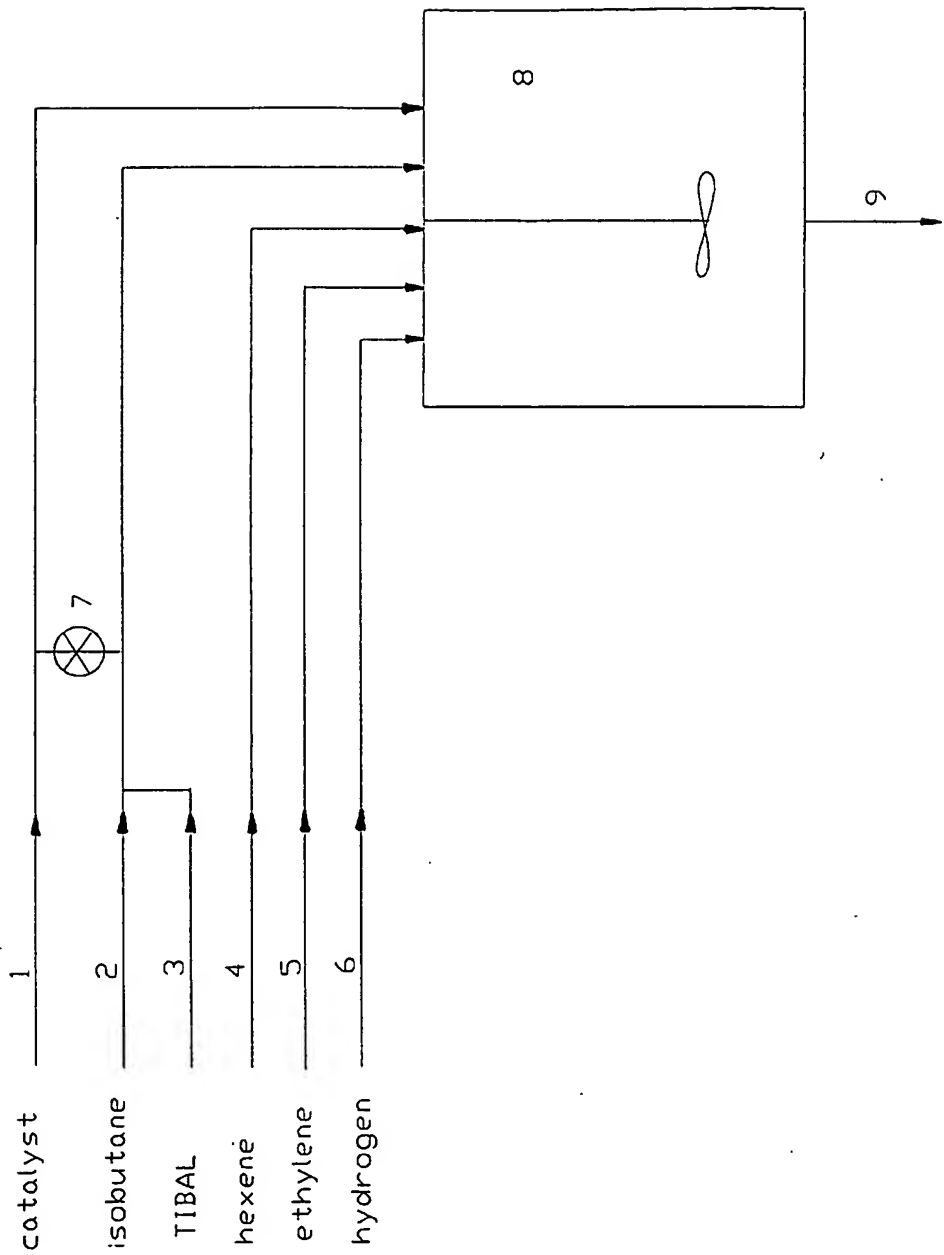


FIG. 1

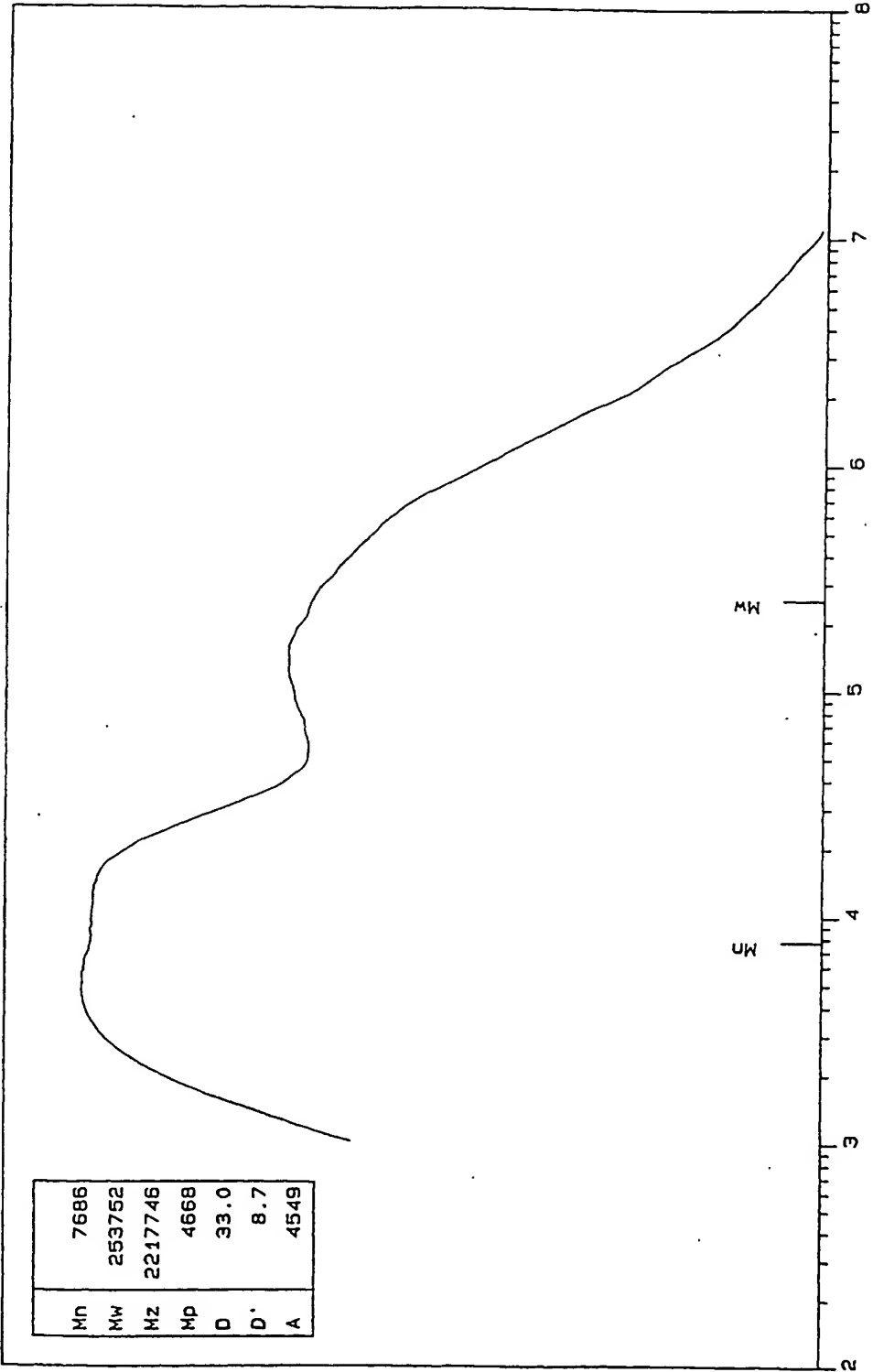


FIG. 2

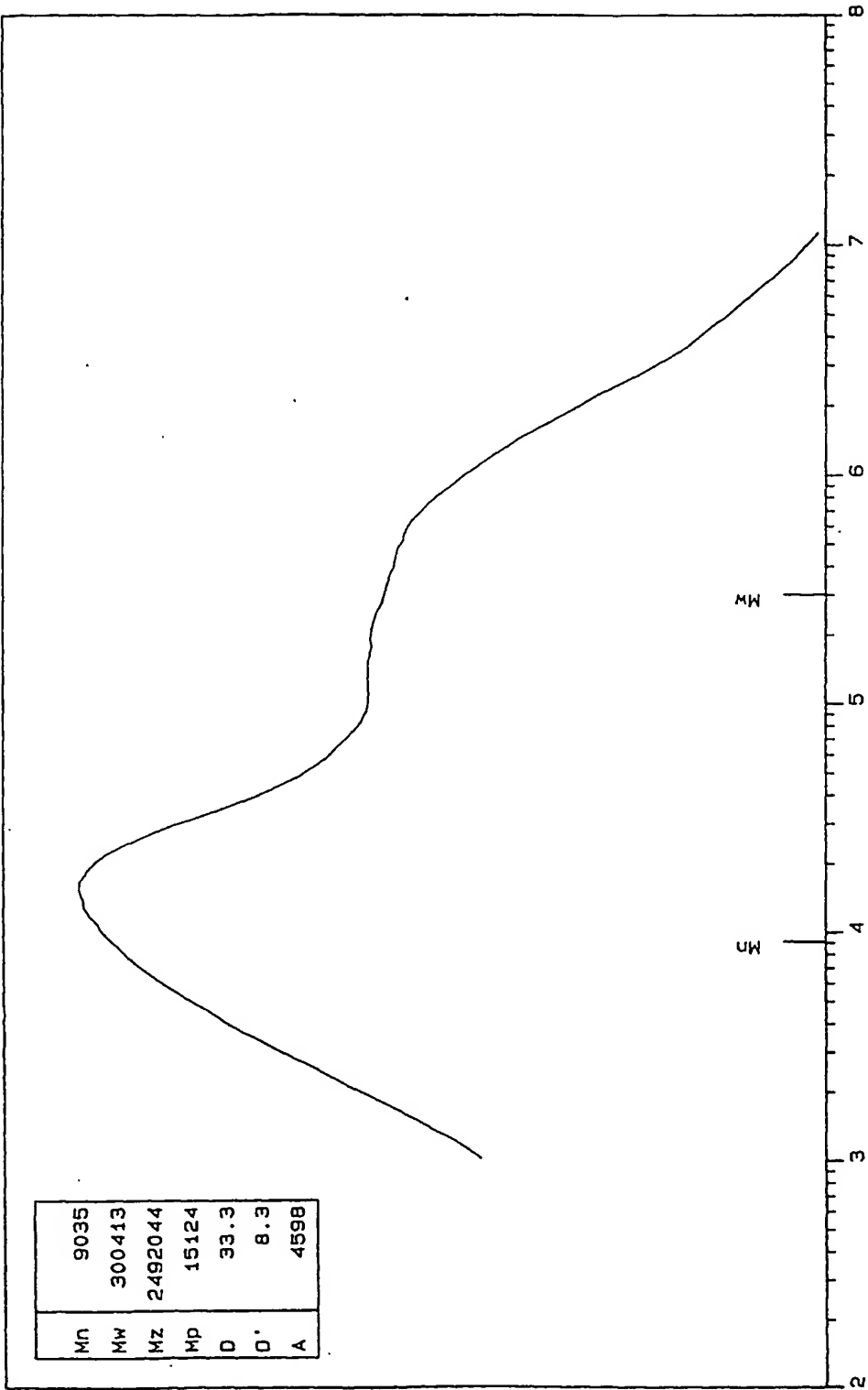


FIG.3

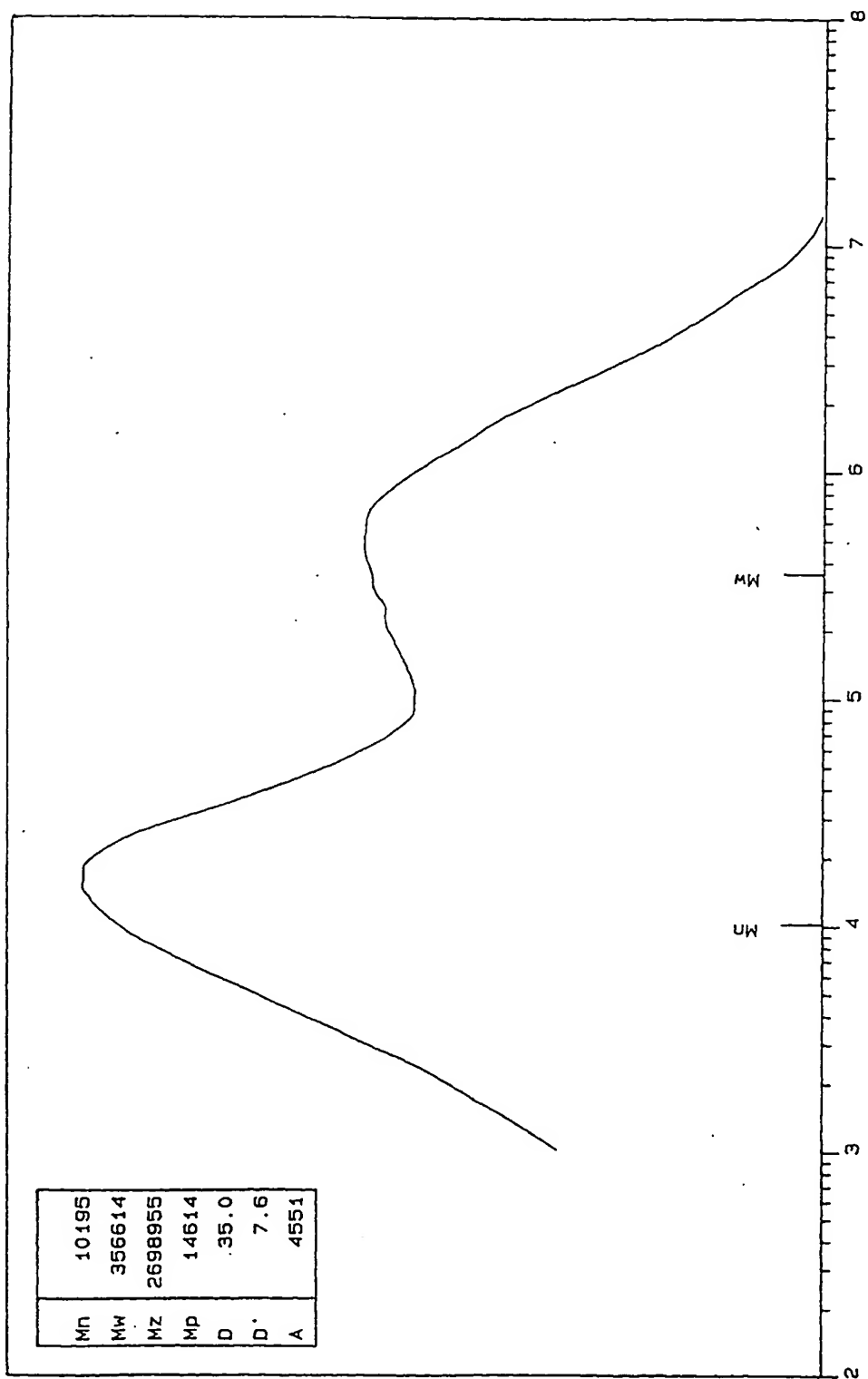


FIG. 4

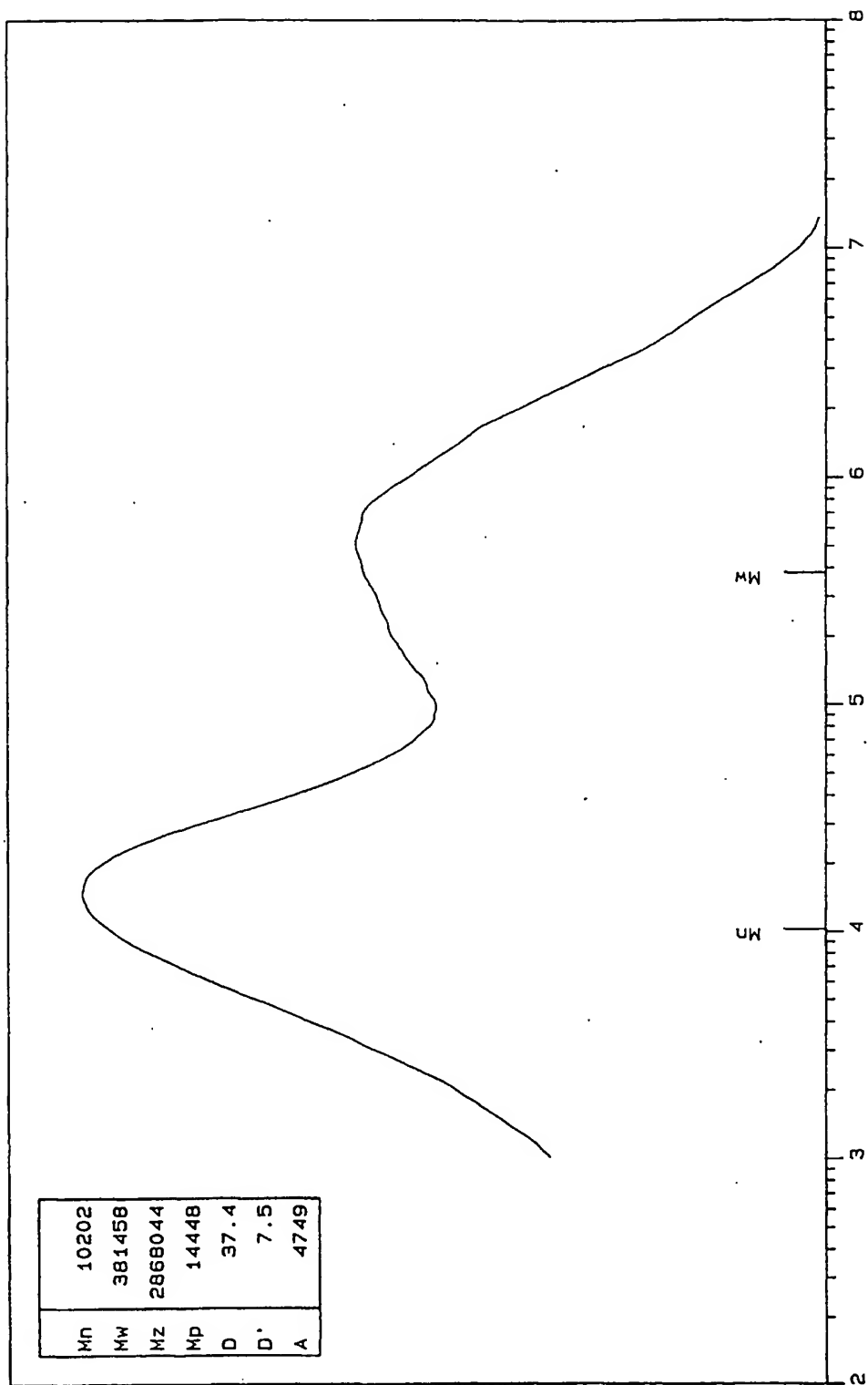


FIG. 5

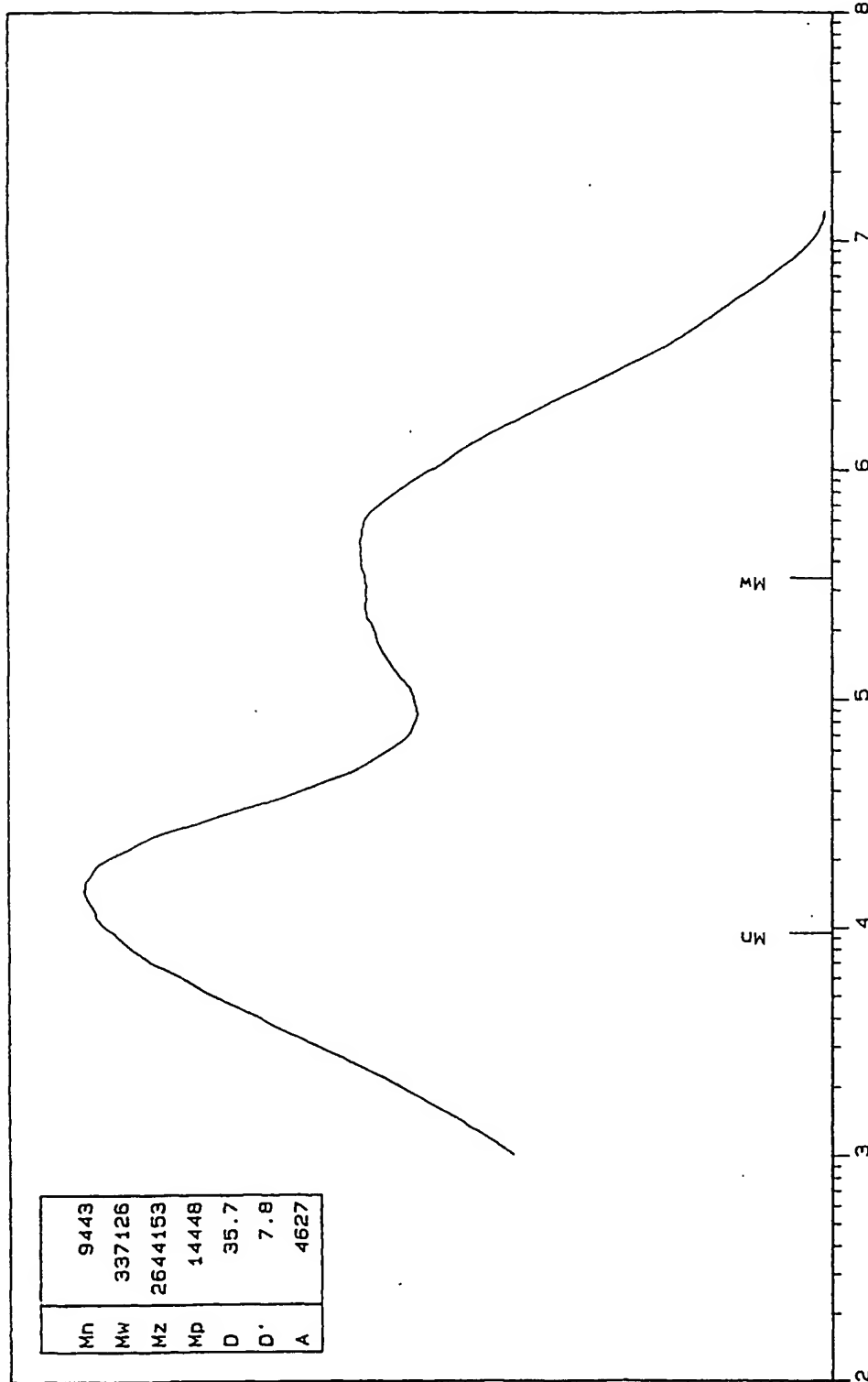


FIG. 6



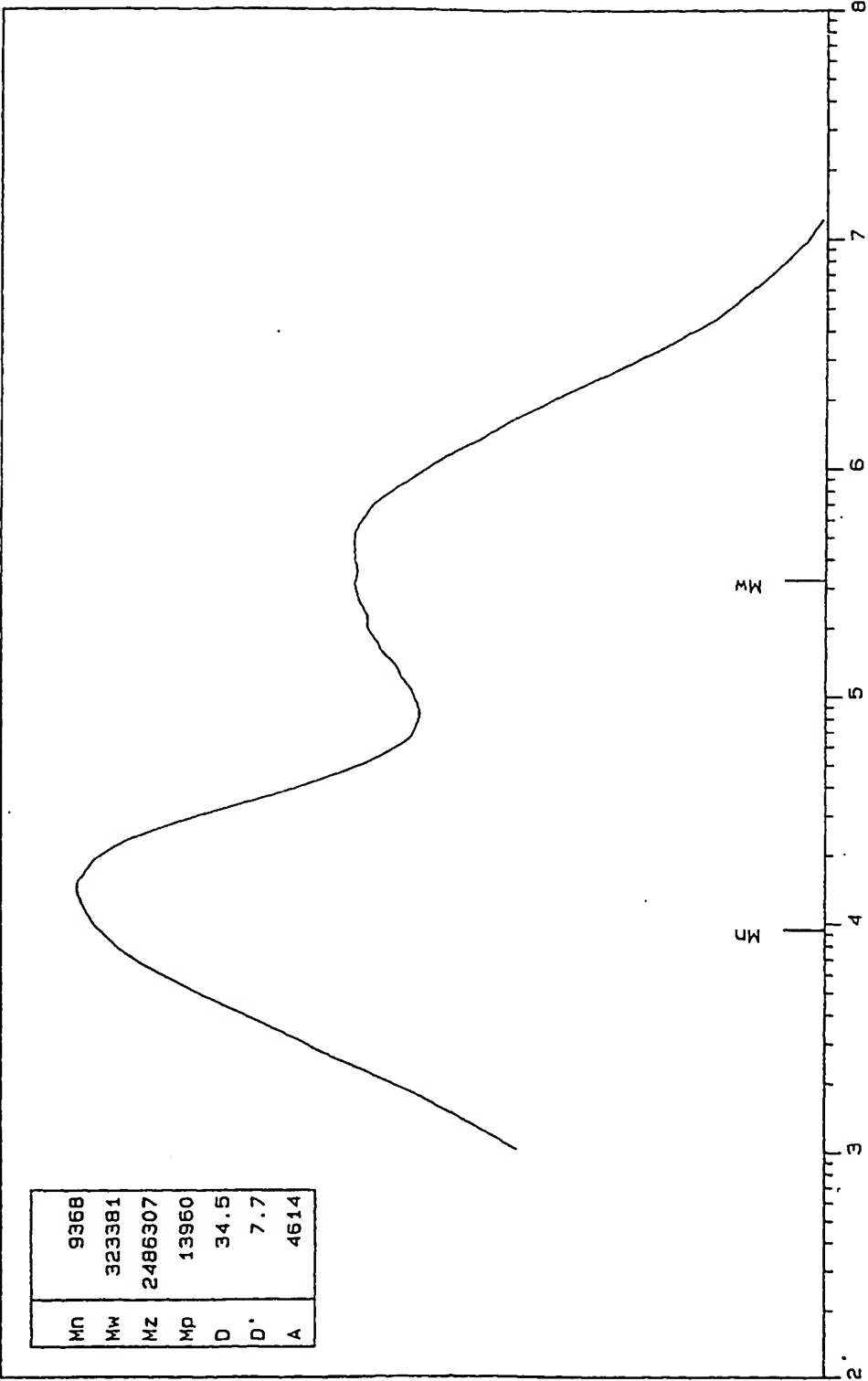


FIG. 7

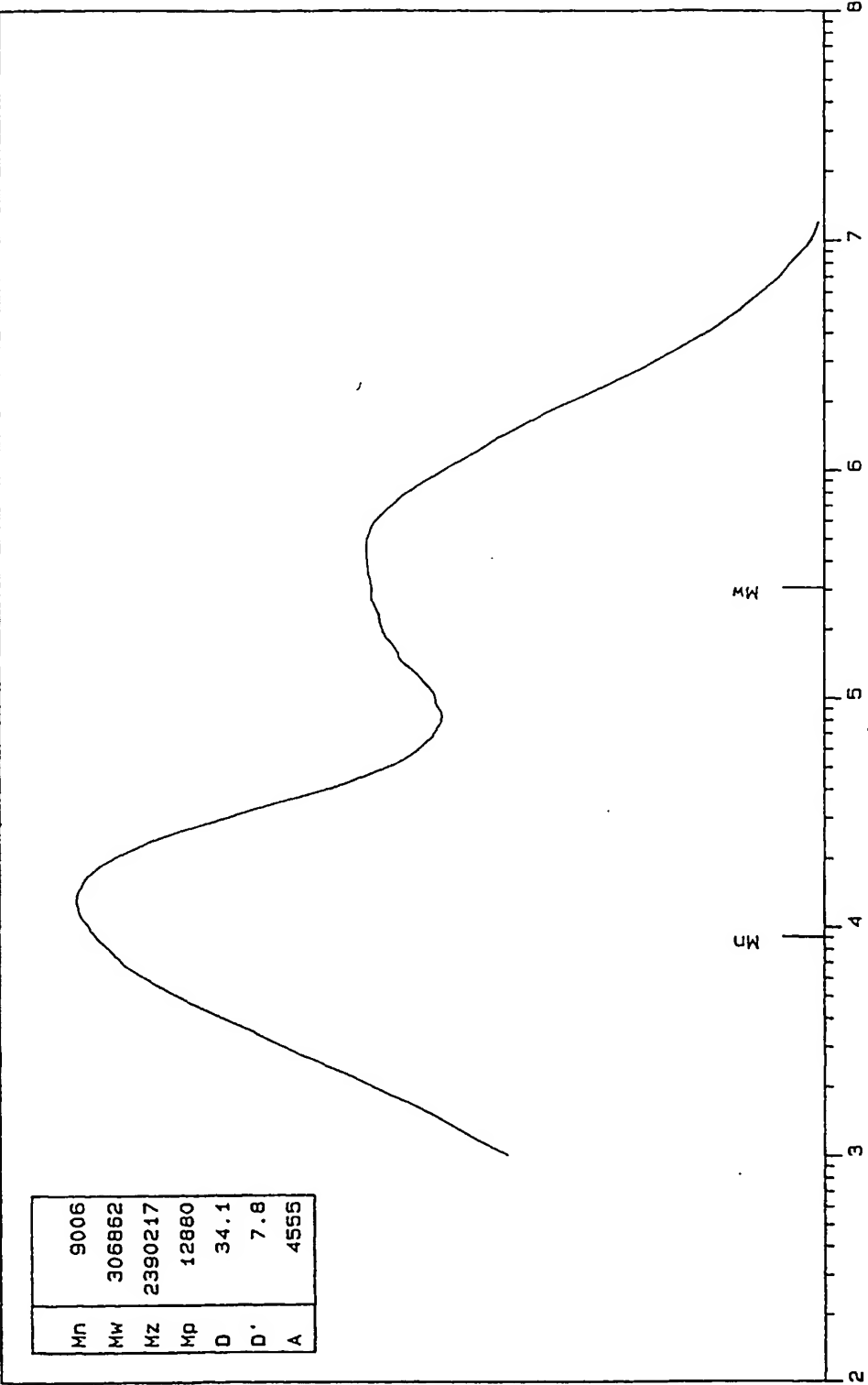


FIG.8

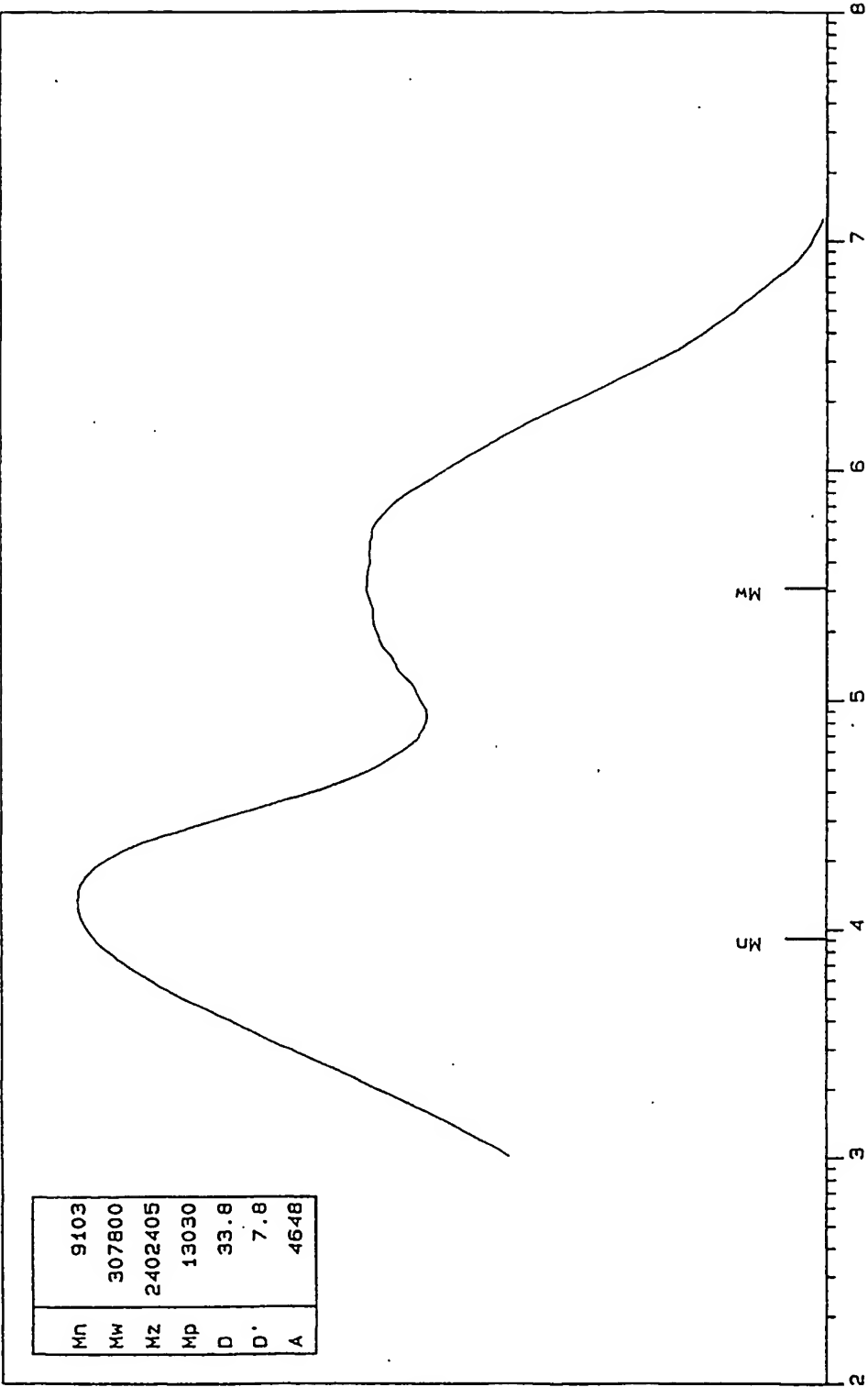


FIG.9

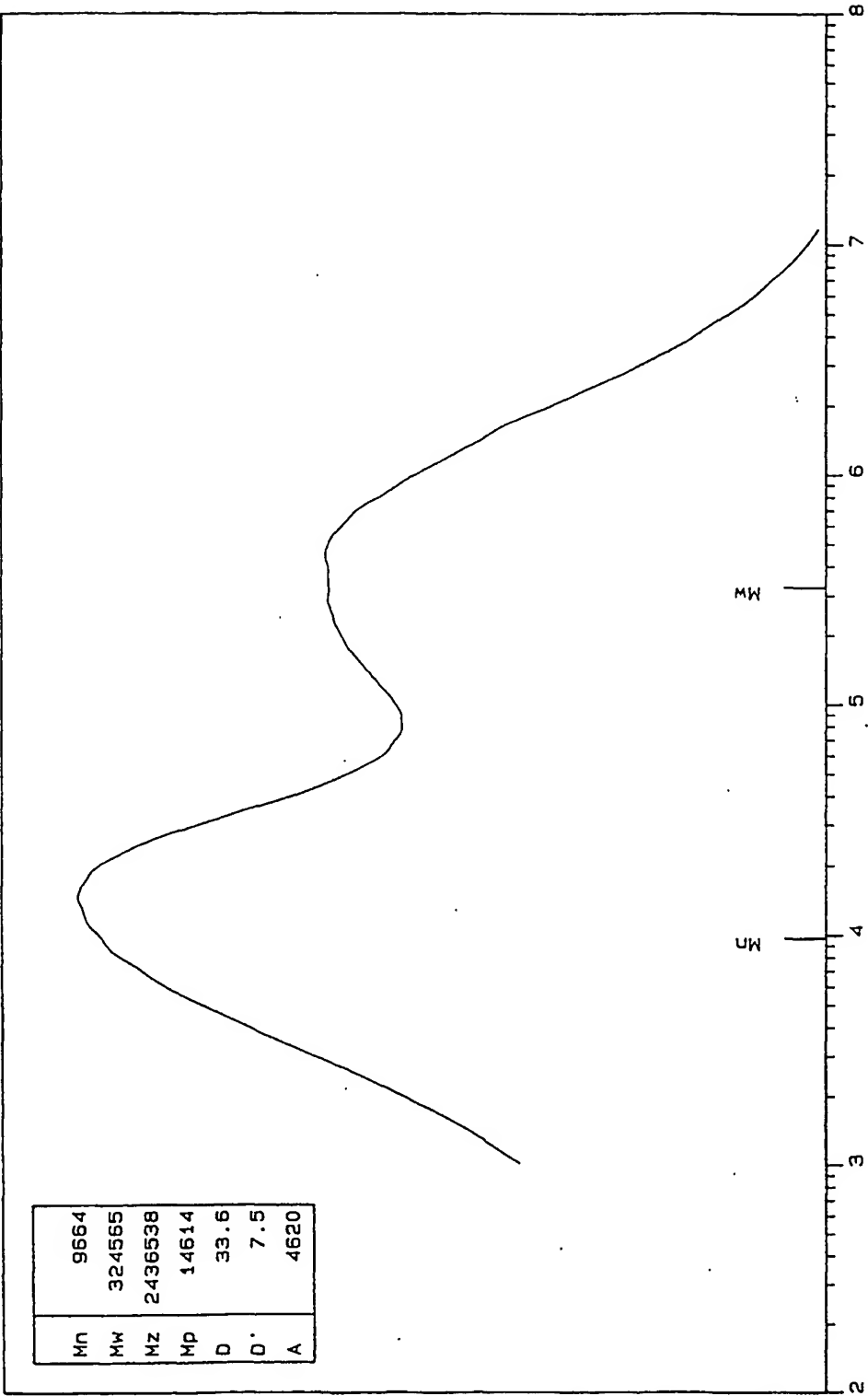


FIG.10

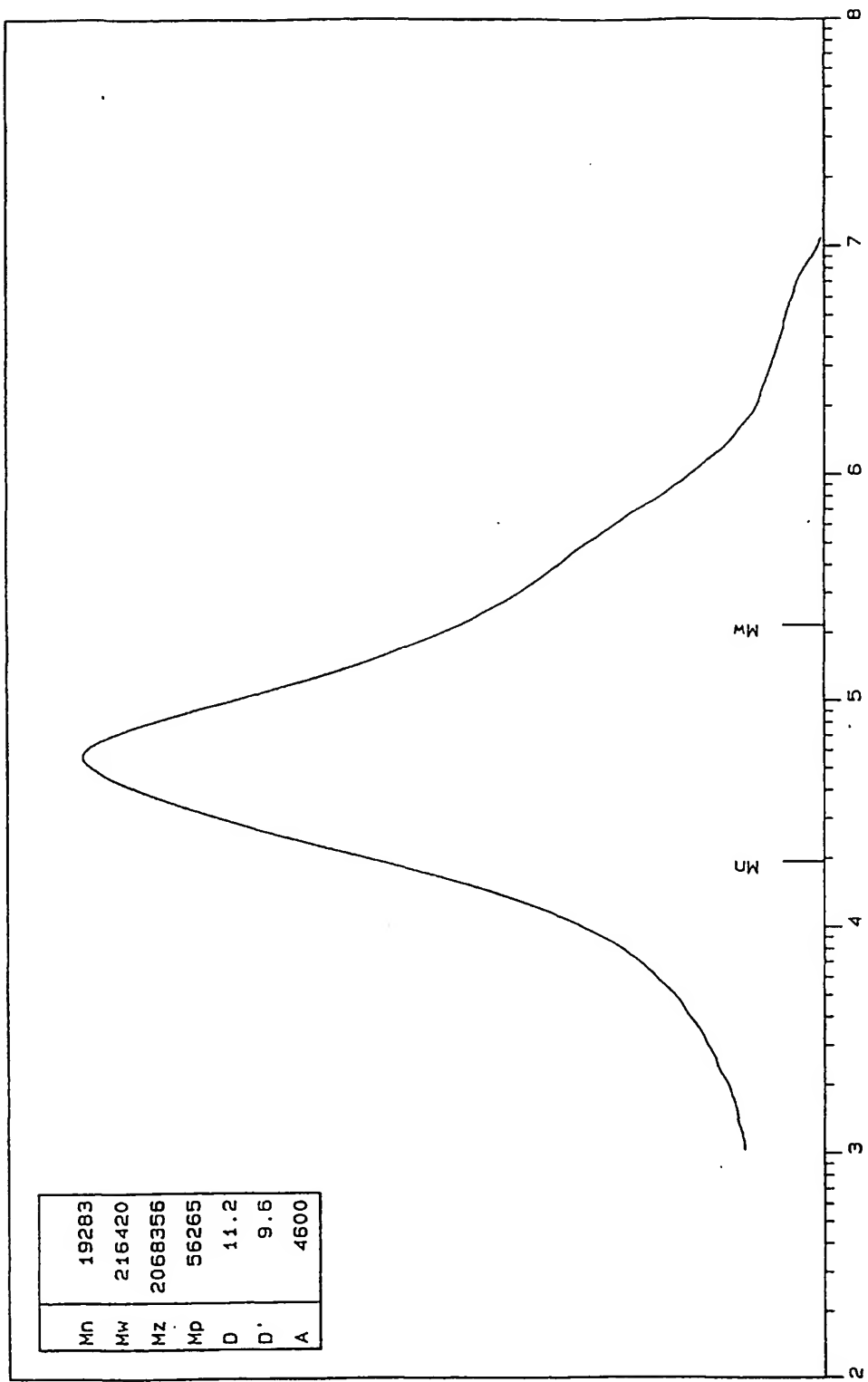


FIG.11

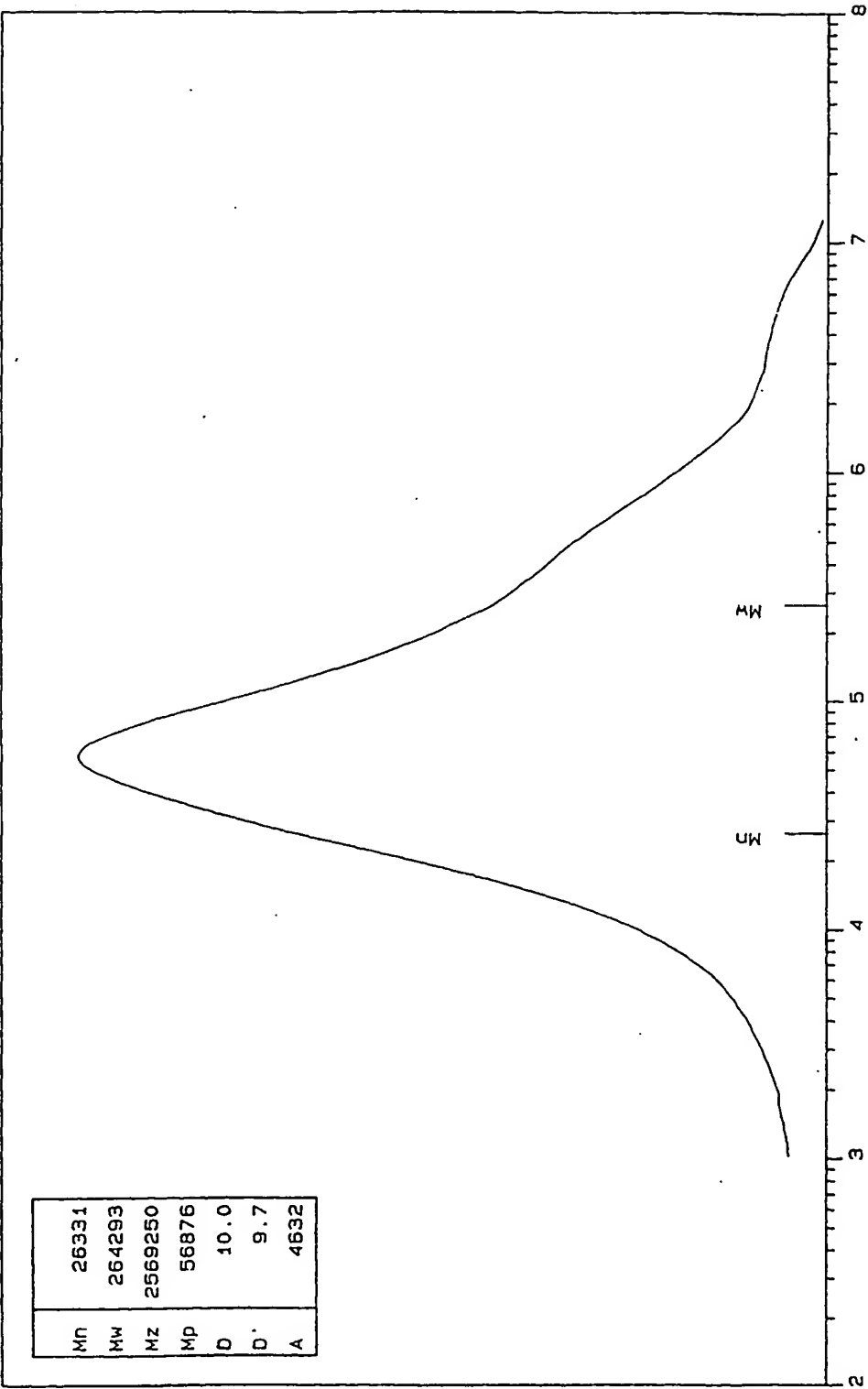


FIG. 12

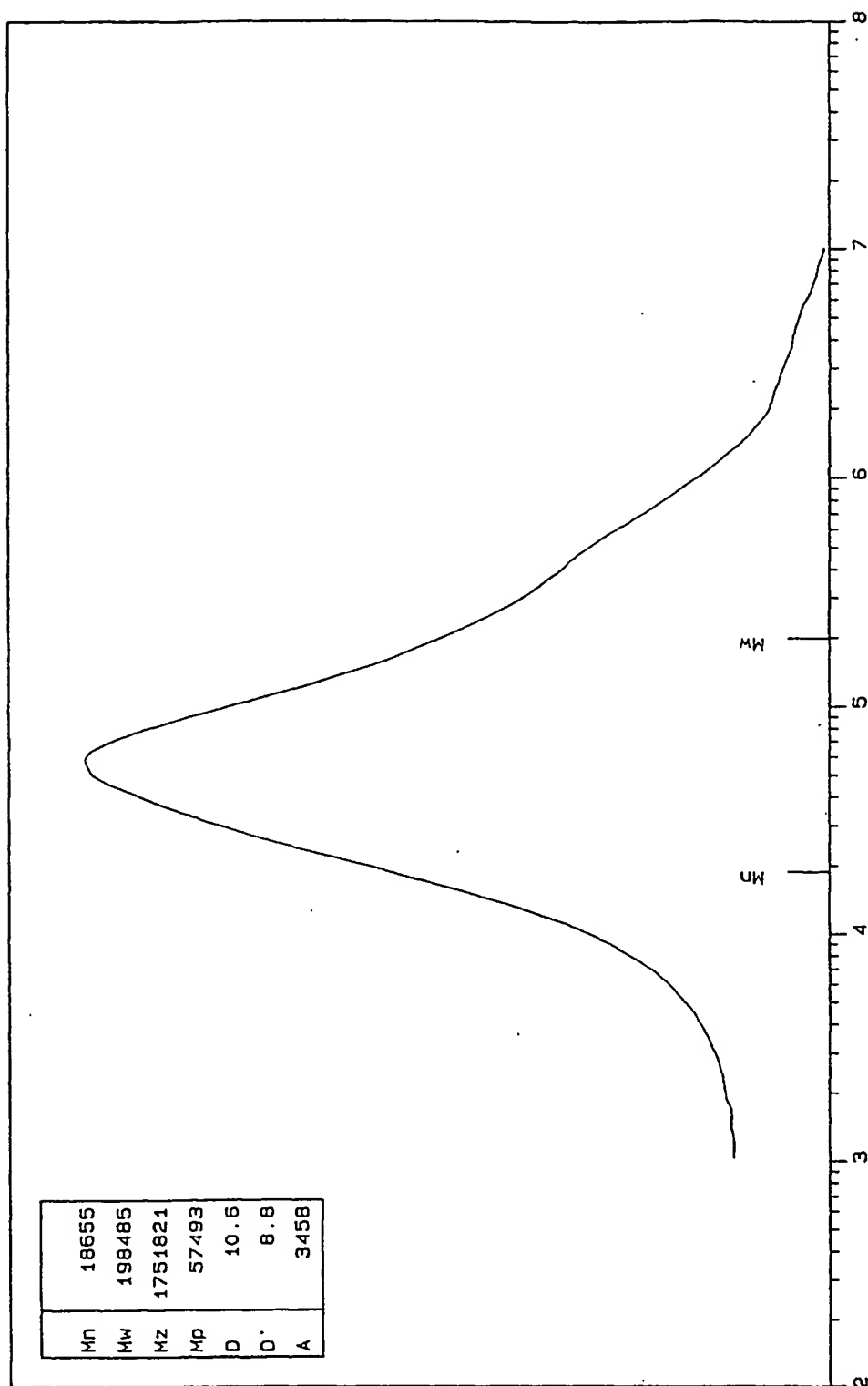


FIG.13

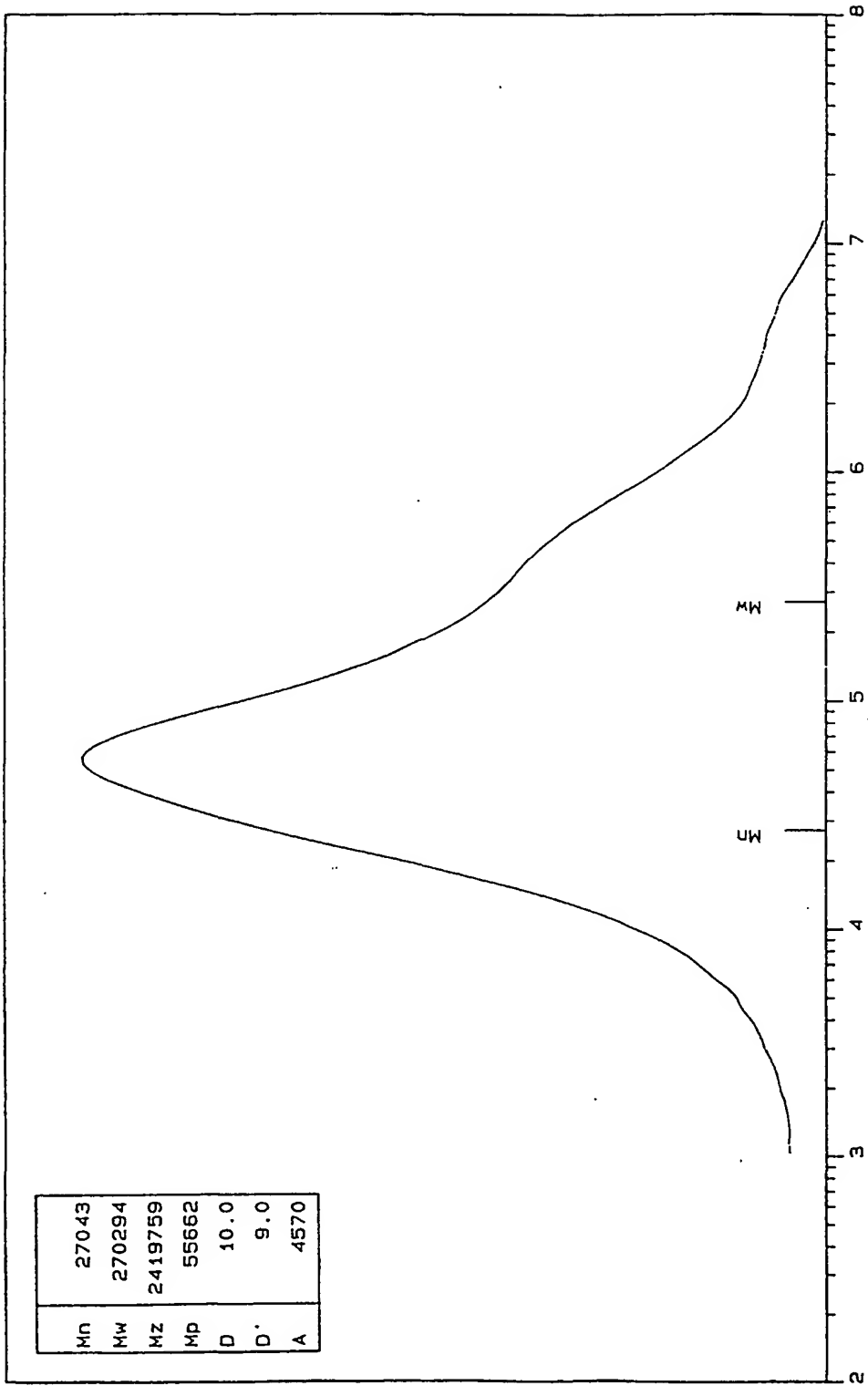


FIG.14



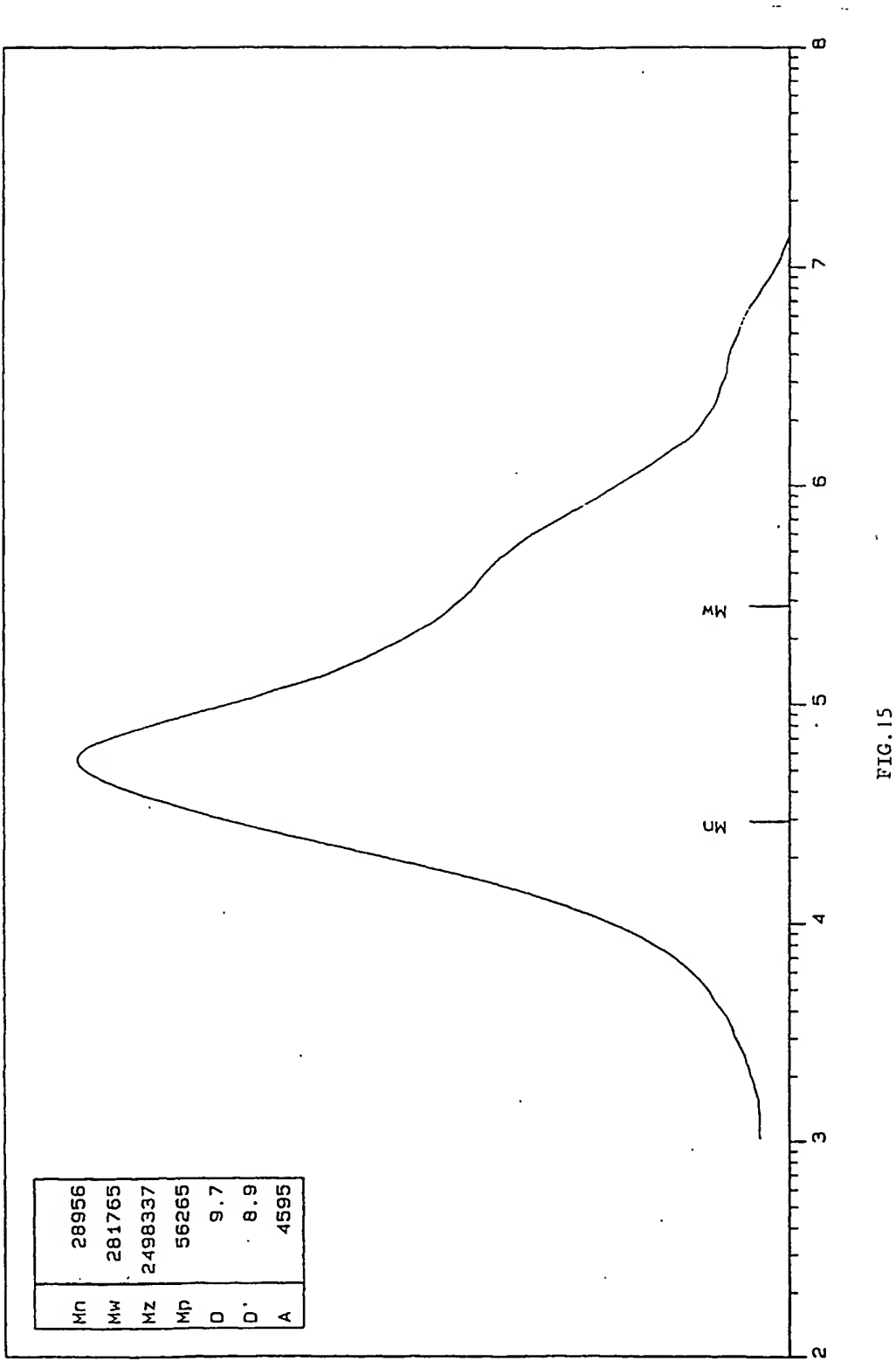


FIG. 15

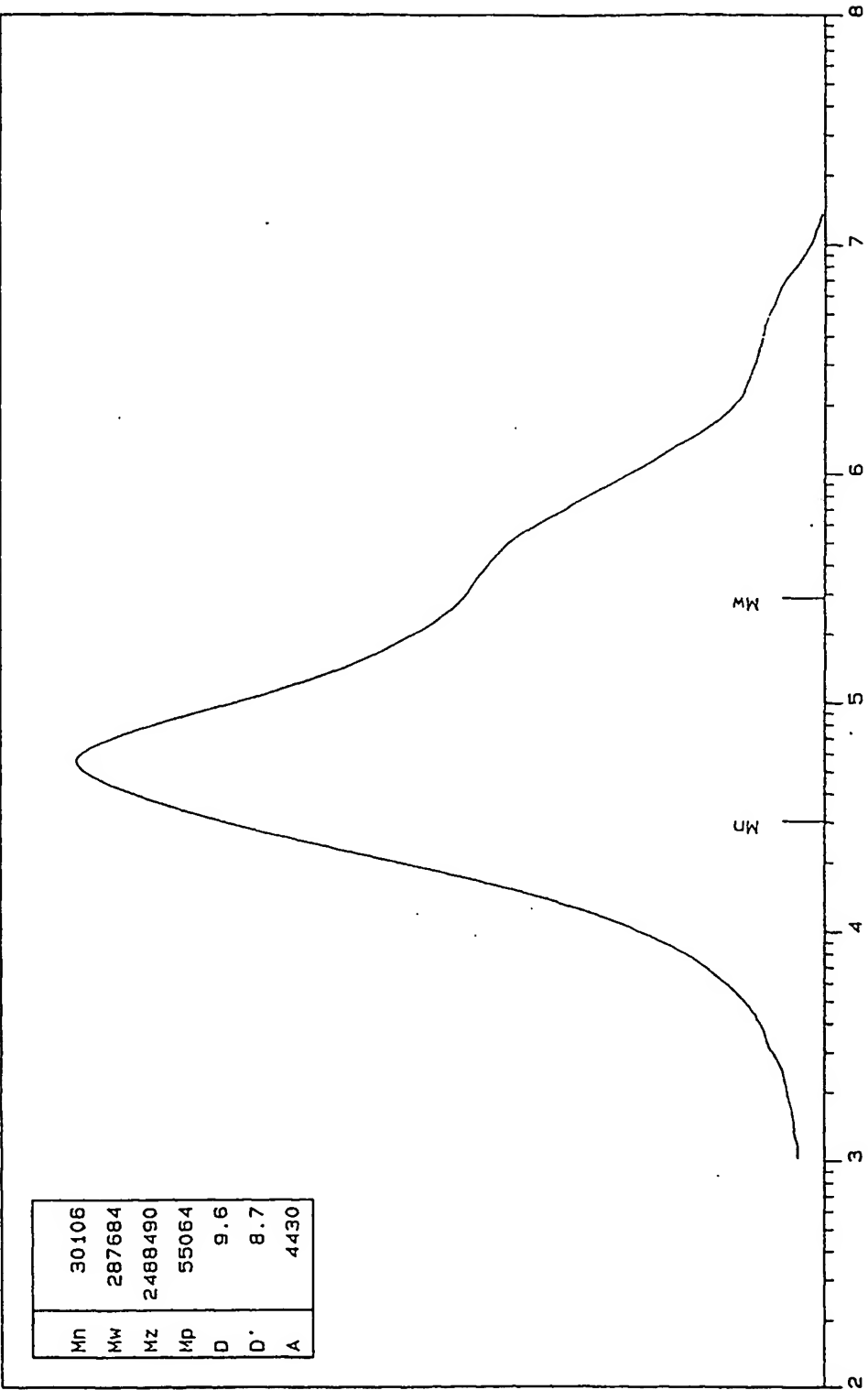


FIG. 16

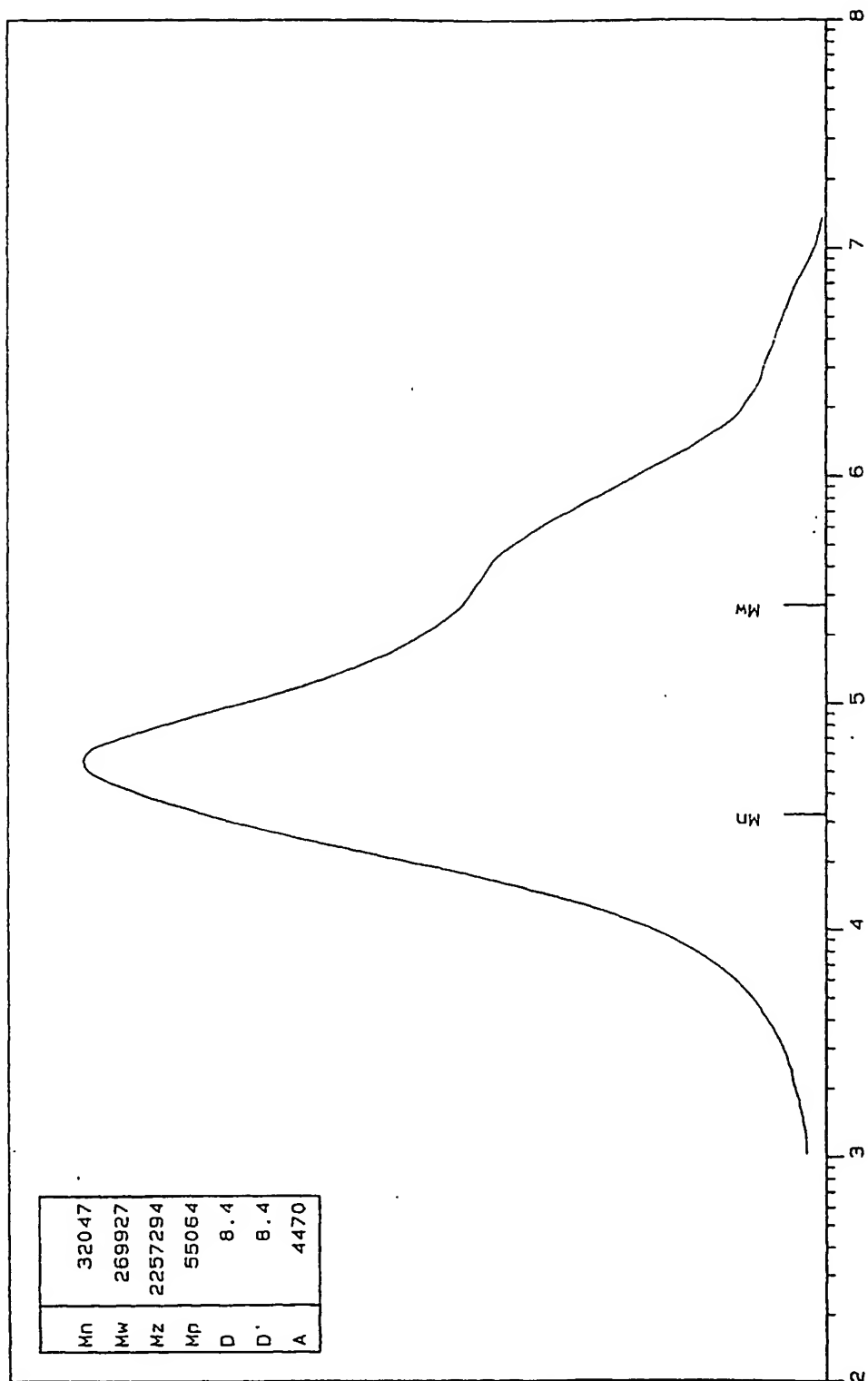


FIG.17

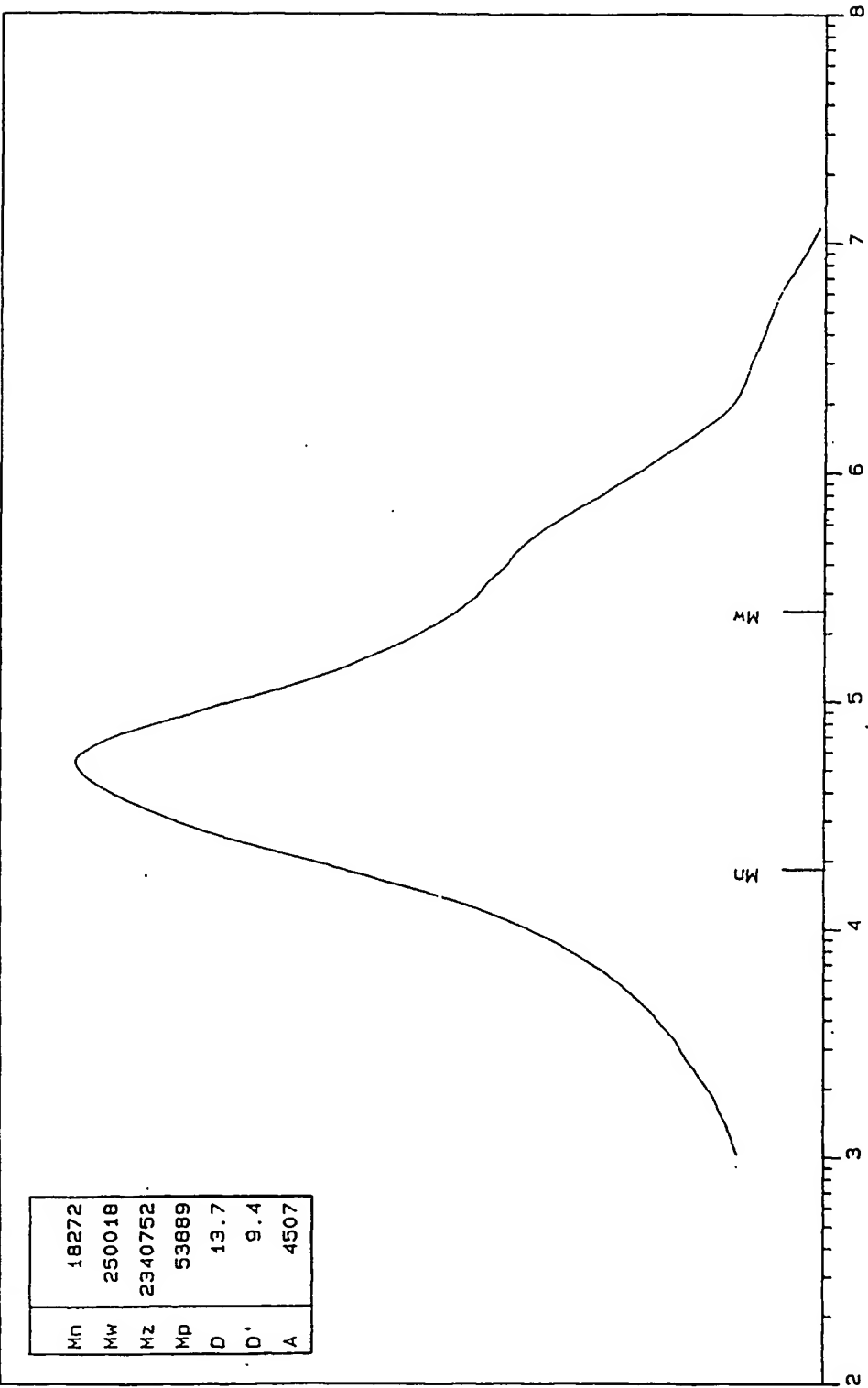


FIG.18

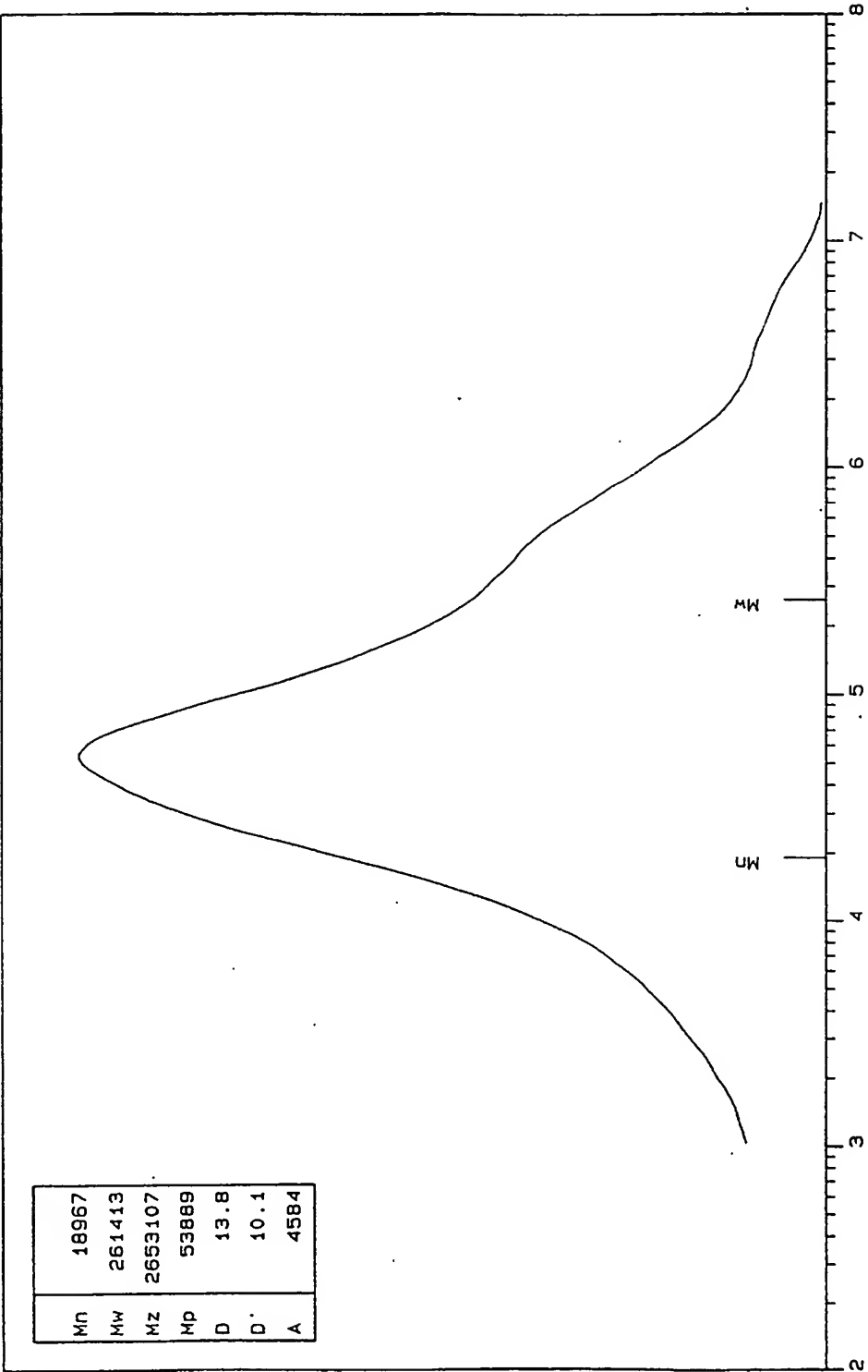


FIG. 19

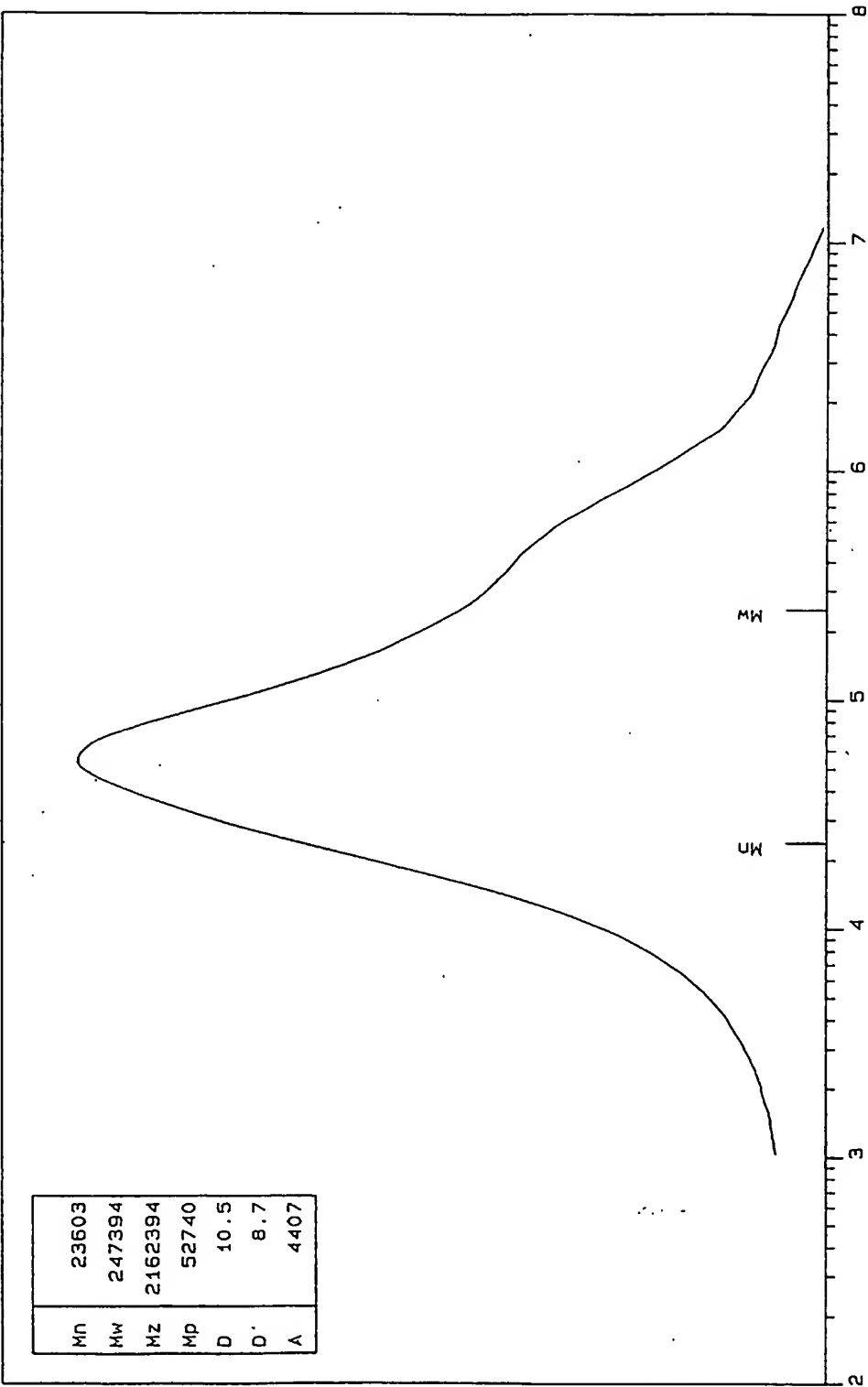


FIG. 20